June, 1990] NOTES *Bull. Chem. Soc. Jpn., 63, 1819—1821 (1990)* 1819

# The Dissociation Equilibrium of the Copper(II) Acetate Dimer in Acetic Acid

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(Received October 4, 1989)

**Synopsis.** The dissociation equilibrium of the copper(II) acetate dimer in acetic acid was studied by means of high-sensitivity spectorophotometry. The dissociation constant of the nonaquated dimer was determined to be $K_{\mathrm{dis}}=10^{-6.2\pm0.2}$ at 25 °C. The dissociation was promoted in the presence of water. The formation constant of the monoaquated monomer was estimated to be $K_{\mathrm{m1}}=3.0$.

It is well known that copper(II) acetate in acetic acid exists in a dimeric structure,[1–4] much as in the crystalline phase. The dissociation of dimeric copper(II) acetate into a monomer is important to the exact treatment of the solution chemistry of copper(II) acetate in acetic acid.[5] The evaluation of the dissociation constant of the dimer has been attempted by several workers.[1–3] The reliable value of the constant has, however, not yet been obtained because of quite large errors in the data.

The spectrophotometric measurement of the absorption of copper(II) acetate is one of the most direct and precise methods for the determination of the dissociation constant.[4] It is, however, quite difficult to obtain a reliable value of the constant by the usual spectrophotometry method because of the relatively low molar extinction coefficient and the small value of the dissociation constant of copper(II) acetate in acetic acid.

Recently, we developed a high-sensitivity spectrophotometer system equipped with a 100 mm flow cell and an external microcomputer.[6] In the present paper, the dissociation equilibrium of copper(II) acetate dimer in acetic acid has been investigated by using this high-sensitivity spectrophotometry. The role of water in the dissociation equilibrium was also discussed.

## Experimental

**Reagents.** The acetic acid and copper(II) acetate were prepared by the methods described elsewhere.[4]

**Instruments and Measurements.** The spectrophotometric measurements were performed with a Hitachi spectrophotometer, model U-3400, equipped with a quartz flow cell (light pass, 100 mm). By means of data processing with an external microcomputer, the uncertainty of absorbance was reduced to ±0.0002. Consequently, the sensitivity of this system was improved about 100 times compared to that of the usual methods.[6]

By means of a Teflon tube, the flow-absorbance cell was connected to a mixing vessel kept at 25.0 °C through a pump. Acetic acid (200 ml) was placed in the mixing vessel, and then an appropriate amount of a copper(II) acetate standard solution ($C_{\mathrm{Cu}}=10^{-2}$ M; M=mol dm$^{-3}$) was successively added. The spectrum of acetic acid was used as a blank spectrum. In order to prevent any bad effects of moisture in air, nitrogen was flowed over the solution.

## Results and Discussion

The absorption spectra of copper(II) acetate, as measured at various copper(II) concentrations, were smoothed, and the drift of the base line was corrected by comparison with the absorbance at 500 nm, at

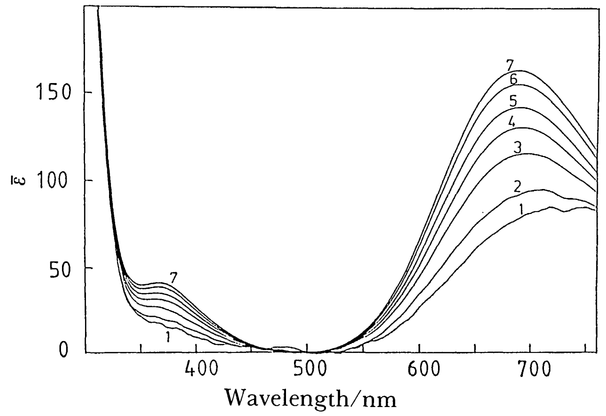

Fig. 1. Absorption spectra of copper(II) acetate in acetic acid at various copper(II) concentrations. $C_{\mathrm{Cu}}$: 1, 1.08; 2, 2.15; 3, 5.37; 4, 10.1; 5, 21.2; 6, 51.4; 7, 98.1×10$^{-5}$ M. $C_{\mathrm{H_2O}}$: 1.15 M.

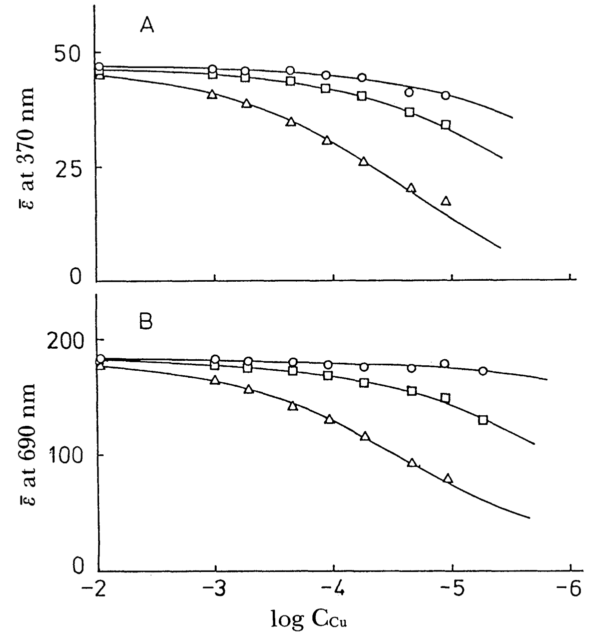

Fig. 2. Apparent molar extinction coefficents, $\bar{\varepsilon}$, at 370 nm (A) and 690 nm (B) of copper(II) acetate in acetic acid containing various amounts of water. $C_{\mathrm{H_2O}}$: ○, 3.45×10$^{-2}$; □, 3.39×10$^{-1}$; △, 1.15 M. Solid lines are the calculated curves by using the parameters listed in Table 1.

which the absorption of copper(II) acetate is negligible. The spectra, converted to an apparent molar extinction coefficient, $\bar{\varepsilon}$ (absorbance per mole of copper(II)), are shown in Fig. 1, where the spectra at $C_{\mathrm{H_2O}}$=1.15 M are depicted as an example. The apparent molar extinction coefficients at 370 nm and 690 nm are plotted in Fig. 2 as a function of the total concentration of copper, $C_{\mathrm{Cu}}$, at various concentrations of water, $C_{\mathrm{H_2O}}$. As can be seen from these figures, reliable absorbance data were obtained down to about $10^{-5}$ M of copper(II), even for the peak at 370 nm with a lower molar extinction coefficient. In the case of the usual spectrophotometry, $10^{-3}$ M of copper(II) acetate is the limit of the concentration at which a reliable absorbance can be obtained at 370 nm.

By considering the side reactions of dimeric and monomeric species of copper(II) acetate with water, the dissociation of the dimer into the monomer is written by;

$$\mathrm{Cu_2(OAc)_4}' \rightleftarrows 2\,\mathrm{Cu(OAc)_2}', \tag{1}$$

where

$$[\mathrm{Cu_2(OAc)_4}'] = \sum_p [\mathrm{Cu_2(OAc)_4(H_2O}_p)], \tag{2}$$

$$[\mathrm{Cu(OAc)_2}'] = \sum_q [\mathrm{Cu(OAc)_2(H_2O}_q)]. \tag{3}$$

The conditional dissociation constant of dimeric copper(II) acetate is defined by;

$$K_{\mathrm{dis}}' = [\mathrm{Cu(OAc)_2}']^2/[\mathrm{Cu_2(OAc)_4}']. \tag{4}$$

An apparent molar extinction coefficient is given by;

$$\bar{\varepsilon} = (2[\mathrm{Cu_2(OAc)_4}']\varepsilon_{\mathrm{d}}' + [\mathrm{Cu(OAc)_2}']\varepsilon_{\mathrm{m}}')C_{\mathrm{Cu}}^{-1} \tag{5}$$

where $\varepsilon_{\mathrm{d}}'$ and $\varepsilon_{\mathrm{m}}'$ are the mean molar extinction coefficients (absorbance per mole of copper(II)) of dimeric and monomeric species of the copper(II) acetate at a given water concentration, respectively. Those values are constant under the conditions of $C_{\mathrm{H_2O}}$=constant.

It is well established that the absorption peak at 370 nm of copper(II) acetate is characteristic of the dimeric structure, and the absorption of the monomeric species at 370 nm is assumed to be negligible ($\varepsilon_{\mathrm{m}}'=0$).[3,4,7] The values of the conditional constants, $K_{\mathrm{dis}}'$, and $\varepsilon_{\mathrm{d}}'$ at each concentration of water were evaluated from the data depicted in Fig. 2(A) with the help of a microcomputer (Table 1). The calculated curves obtained by using these constants are shown by solid lines in Fig. 2(A). The values of the mean molar extinction coefficients of the dimeric ($\varepsilon_{\mathrm{d}}'$) and monomeric ($\varepsilon_{\mathrm{m}}'$) species at 690 nm were determined by using the values of $K_{\mathrm{dis}}'$ determined at 370 nm (Table 1). The curves calculated by using the values of $\varepsilon_{\mathrm{m}}'$ and $\varepsilon_{\mathrm{d}}'$ at 690 nm thus obtained are shown by solid lines in Fig. 2(B).

In order to examine the effect of water on the dissociation equilibria in detail, the change in the absorption spectrum of copper(II) acetate was measured by the successive addition of water. As can be seen from Table 1, the value of the mean molar extinction coefficient of dimeric species, $\varepsilon_{\mathrm{d}}'$, at 370 nm is constant, independent of the water concentration.

Table 1. The Logarithmic Conditional Dissociation Constants and Mean Molar Extinction Coefficients of the Copper(II) Acetates in Acetic Acid at 25.0 °C

| $C_{\mathrm{H_2O}}$/M | $\log K_{\mathrm{dis}}'$ | 370 nm $\varepsilon_{\mathrm{d}}'$ | 690 nm $\varepsilon_{\mathrm{m}}'$ | 690 nm $\varepsilon_{\mathrm{d}}'$ |
|---|---|---|---|---|
| $3.45\times10^{-2}$ | $-6.2\pm0.2$ | 47 | 120 | 184 |
| $3.39\times10^{-1}$ | $-5.6\pm0.2$ | 47 | 44 | 184 |
| 1.15 | $-4.5\pm0.2$ | 47 | 32 | 184 |

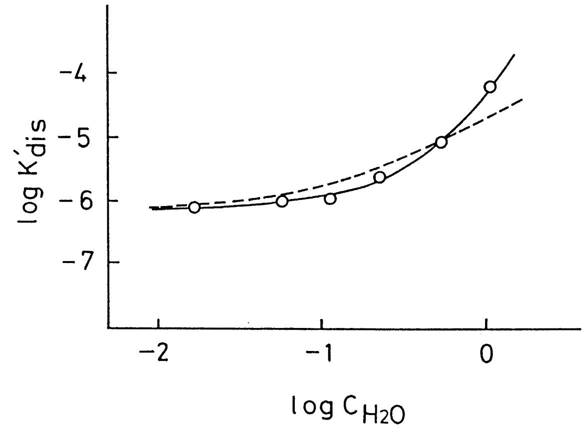

Fig. 3. The conditional dissociation constant of copper(II) acetate in acetic acid as a function of water concentration. $C_{\mathrm{Cu}}$: $1.33\times10^{-5}$ M. Broken line and solid line are calculated curves. See text.

The conditional dissociation constant of dimeric copper(II) acetate, $K_{\mathrm{dis}}'$, at each water concentration was evaluated from the apparent molar extinction coefficient, $\bar{\varepsilon}$, at 370 nm by using the values of $\varepsilon_{\mathrm{d}}'=47$ and $\varepsilon_{\mathrm{m}}'=0$. The values of $\log K_{\mathrm{dis}}'$ thus obtained are plotted as a function of $\log C_{\mathrm{H_2O}}$ in Fig 3.

The dissociation of the copper(II) acetate dimer to the monomer and an aquation of these species are generally written by the use of Scheme 1. The formation constant of the monoaquacomplex of the dimer has been obtained as $K_{\mathrm{d1}}=0.6$ by using the statistical assumption for the diaquacomplex of $K_{\mathrm{d2}}=1/4\,K_{\mathrm{d1}}$.[8]

If we assume the formation of only a monoaquacomplex for the monomeric species, $\mathrm{Cu(OAc)_2(H_2O)}$, the conditional dissociation constant defined by Eq. 4 is written by Eq. 6 by using the above assumption,

$$\begin{tikzcd}
\mathrm{Cu_2(OAc)_4+2H_2O} \arrow[r, shift left, "K_{\mathrm{dis}}"] \arrow[d, shift left, "K_{\mathrm{d1}}"] & \mathrm{2\,Cu(OAc)_2+2H_2O} \arrow[l, shift left] \arrow[dd, shift left, "K_{\mathrm{m1}}"] \\
\mathrm{Cu_2(OAc)_4(H_2O)+H_2O} \arrow[u, shift left] \arrow[d, shift left, "K_{\mathrm{d2}}"] & \\
\mathrm{Cu_2(OAc)_4(H_2O)_2} \arrow[u, shift left] \arrow[r, shift left, "K_{\mathrm{dis(W)}}"] & \mathrm{2\,Cu(OAc)_2(H_2O)} \arrow[l, shift left] \arrow[uu, shift left]
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{Cu(OAc)_2(H_2O)_{(\mathit{n}-1)}+H_2O} \arrow[d, shift left, "K_{\mathrm{m}n}"] \\
\mathrm{Cu(OAc)_2(H_2O)}_n \arrow[u, shift left]
\end{tikzcd}$$

Scheme 1.

$K_{d2}=1/4\,K_{d1}$;

$$K_{dis}'=K_{dis}\left(\frac{1+K_{m1}[H_2O]}{1+1/2\,K_{d1}[H_2O]}\right)^2 \qquad (6)$$

where $K_{dis}$ refers to the dissociation constant between nonaquated species, $K_{dis}=[Cu(OAc)_2]^2[Cu_2(OAc)_4]^{-1}$, and where $K_{m1}$ refers to the formation constant of the monoaquacomplex of monomeric copper(II) acetate. The broken line in Fig. 3 is the calculated curve giving the minimum discrepancy from the experimental results. As can be seen from Fig. 3, no value of $K_{m1}$ reproduces the experimental results. The slope of the plots goes up to over 3 at higher water concentrations. These facts indicate that the monomeric complex forms aquated species higher than the monoaquacomplex ($n>1$).

The information obtained from the results shown in Fig. 3 is too sparse to determine independently the stepwise constants of the aquation of monomeric species. If we assume a statistical correlation[9] for the successive substitution of four solvent acetic acid molecules coordinating to the monomeric copper(II) acetate by means of water molecules, the successive aquation constants are given by $K_{m2}=3/8\,K_{m1}$, $K_{m3}=4/9\,K_{m2}$, and $K_{m4}=3/8\,K_{m3}$. By using this assumption, the value of the formation constant of the monoaquacomplex giving the minimum discrepancy was evaluated as $K_{m1}=3.0$. As can be seen from Fiq. 3 (solid line), the calculated curve shows a good fitting with the experimental results. The aquation constant of copper(II) acetate obtained here ($K_{m1}=3.0$) is of the same order of magnitude as that of other acetates of divalent transition metals in acetic acid ($K_{m1}=1.6$, 6.7, and 3.1 for Mn(II), Co(II), and Zn(II) acetates respectively).[8]

As can be seen from Fig. 3, $K_{dis}'$ is constant irrespective of the water concentration at low $C_{H_2O}$ values. As the formation of aquated species is negligible in this region, $K_{dis}'$ corresponds to $K_{dis}$. Thus, the dissociation constant of non-aquated species is obtained as $K_{dis}=10^{-6.2\pm0.2}$. Recently, the dissociation constant of copper(II) acetate in acetic acid was estimated theoretically from the partition data of copper(II) carboxylates with the help of regular solution theory.[10] The value thus estimated, $K_{dis}=10^{-6.09}$, agrees well with the value obtained here.

The dissociation constant of the aquated copper(II) acetate dimer defined by Eq. 7 is calculated as $K_{dis(w)}=10^{-4.2}$;

$$K_{dis(w)}=\frac{[Cu(OAc)_2(H_2O)]^2}{[Cu_2(OAc)_4(H_2O)_2]}=K_{dis}\frac{K_{m1}^2}{K_{d1}K_{d2}}. \qquad (7)$$

This value indicates that the dissociation of an aquated dimer is one hundred times easier than that of a non-aquated species.

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